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A STUDY OF THE HYDROLYSIS OF THE HEXACHLOROANTIMONATE(V)
AND HEXAFLUOROANTIMONATE(V) IONS IN SOLUTIONS

A THESIS

Presented to
the Faculty of the Graduate Division

by
William Anthony Mazeika

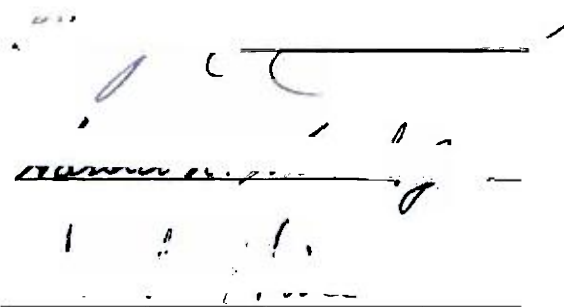
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Approved:

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Date Approved by Chairman:

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SUMMARY

The purpose of this investigation is to study the rates of hydrolysis of SbCl_6^- and SbF_6^- . In order to determine the effects of acid and base on the hydrolysis rate, the reaction is followed in media of varying pH. The half-times for hydrolysis are calculated and several mechanisms are proposed consistent with the data.

A spectrophotometric method is utilized for following the hydrolysis of SbCl_6^- , i.e., a stock solution of commercial SbCl_5 in HCl is injected into a buffered media and its absorption is determined on a Beckman spectrophotometer. The absorption is proportional to the concentration of SbCl_6^- ; therefore, the rate of hydrolysis can be calculated from the slope when absorption of SbCl_6^- is plotted against time.

Since SbF_6^- does not absorb ultra-violet radiation as does SbCl_6^- , the spectrophotometric method possible with the latter cannot be used with the former. The rate of reaction of SbF_6^- is followed by titration of the released fluoride ion. The method requires that SbF_6^- be introduced as a solid salt, consequently KSbF_6 is dissolved in the various media. The rates of hydrolysis for each step are determined through resolution of the plotted data.

The chief difference in the two systems is that in the chloro case the first step of hydrolysis is measurable and the following steps are very rapid while in the fluoro case the first step is very rapid and the second and third steps are measurable. The

fourth step probably can be measured but this would require a method which distinguishes between species. In acid media the reaction of SbF_6^- is found to be terminated after the fourth step due to the formation of a polymeric substance. In basic media the reactions are rapid and complete.

The difference in the two systems might well be due to differing tendencies to react via an $\text{S}_\text{N}1$ as opposed to an $\text{S}_\text{N}2$ mechanism. Although the various mechanisms may be operative in both systems, it is suggested that the major paths of reaction are different. To evaluate the likelihood of reactions through the various paths the octahedral species are considered from the point of view of whether the complex is more likely to undergo increase or decrease in coordination number. Our experiments, in conjunction with previous works which are cited, suggest that SbF_6^- reacts via an $\text{S}_\text{N}2$ mechanism while SbCl_6^- reacts via an $\text{S}_\text{N}1$ mechanism. Further, the product of the first step in both cases has increased $\text{S}_\text{N}1$ and decreased $\text{S}_\text{N}2$ probability because of inductive and electron release effects.

CHAPTER I

INTRODUCTION

In recent years there has been considerable interest in the replacement reactions of complex ions. Most of the work to date has been concerned with studying complexes in which the central atom is a transition metal with a coordination number of six, and in which the ligands are arranged in octahedral configuration about the central atom. Reviews on this subject are available (1).

Systems which are of comparable interest, but which have received little attention, are those octahedral complexes in which the central atom is a regular element. There are only two detailed studies; that by Neumann and Ramette on the hydrolysis of SbCl_6^- in acid solution (2), and that by Craddock and Jones (3) on the hydrolysis of the catechol complex of arsenic(V). In addition Dess and Parry (4) report some limited observations on AsF_6^- and AsF_5OH^- . The small number of cases studied is in part due to the fact that few such complexes have measurable rates of reaction. From the available information the antimony(V) complexes appear to meet the requirements of having an octahedral configuration and of having measurable rates.

The primary purpose of this study is to investigate the general features of the hydrolysis of SbF_6^- . Among the features of interest are the comparative rates at which the six fluorides are replaced,

and the dependence of these rates on the pH of the solution. In addition, the rate of hydrolysis of SbCl_6^- in the basic region and in the higher pH range of the acidic region has been studied. This study, in conjunction with the work of Neumann and Ramette (2), who studied the hydrolysis of SbCl_6^- in acid solution, is utilized in comparing the hydrolysis of the SbCl_6^- and SbF_6^- ions.

Structures in the Solid State.--Before proceeding to a consideration of the hydrolysis reaction itself, the evidence relating to the structure of complexes containing antimony(V) will be reviewed briefly.

Before 1933, the formulae for antimonates were written in a manner suggesting similarity to pyrophosphates and pyroarsenates, despite the absence of isomorphism. For example, potassium antimonate was written as $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$. In 1929 Hammett (5) pointed out that the well known sodium antimonate has exactly the right content of water to be $\text{NaSb}(\text{OH})_6$. In 1933 Pauling (6) generalized this view by pointing out that the majority of crystallized antimonates contain enough water to correspond to the formula $\text{MSb}(\text{OH})_6$, though some contain additional water of crystallization. The coordination number of six is also consistent with his calculation of the size of the $\text{Sb}(\text{V})$ cation and the OH^- anion. Since that time the formula for antimonic acid has been generally accepted to be $\text{HSb}(\text{OH})_6$, and that for antimonate ion to be $\text{Sb}(\text{OH})_6^-$. Recently Jain and Banerjee (7) supported the formula for the acid by demonstrating that the acid is monobasic.

Concrete evidence for the six-coordinate nature of $\text{Sb}(\text{V})$ in

crystalline solids comes from x-ray studies. In Table I are listed the compounds that have been examined by x-ray methods. For those compounds in which the cation has a single positive charge the lattice is basically of the NaCl or CsCl type. For example, the fluoantimonates of Tl^+ , NH_4^+ , Rb^+ , and Cs^+ form rhombohedra that are slightly distorted CsCl lattices having crystal angles of $96^\circ 0'$, $96^\circ 30'$, $96^\circ 30'$, and $96^\circ 54'$ respectively, rather than the 90° of the CsCl lattice. From the cell constants and the known radii of Tl^+ , Rb^+ , and Cs^+ , it is possible to calculate that the SbF_6^- ion is equivalent to a spherical ion with a radius of about 2.95 \AA in these lattices.

The orientation of the SbX_6^- unit within the lattice may reduce the symmetry from that of the basic NaCl or CsCl type. For example, although KSbF_6 has the cubic body-centered lattice of CsCl, its unit cell contains eight molecules, and it has only the symmetry of the class T_h , in which the three fourfold axes of cubic holohedrism have become twofold axes (8).

A more difficult question to answer experimentally, but one which is more pertinent to the problem at hand, is whether the six groups about the antimony form a perfect or a distorted octahedron. Schrewelius (9), while determining the structure of NaSbF_6 , stressed the point that the exact arrangement of the fluoro ligands was not proven; however, it was plausible that the structure was an NaCl type lattice with the following atom to atom distances: Sb-F, 1.95; Na-F, 2.32; F-F within SbF_6^- octahedra, 2.67 and 2.78; and F-F in adjacent octahedra, 2.72 \AA . It is interesting to note that the F-F distances

Table I
Crystal Structure of Several Antimonates(V)

<u>Compound</u>	<u>Crystal form</u>	<u>Reference</u>
NaSb(OH)_6	tetragonal	(9)
LiSb(OH)_6	tetragonal	(9)
AgSb(OH)_6	tetragonal	(9)
$[\text{Ba(H}_2\text{O)}_2][\text{Sb(OH)}_6]_2$	monoclinic pseudorhombic	(34)
$[\text{Ni(H}_2\text{O)}_6][\text{Sb(OH)}_6]_2$	trigonal	(36)
$[\text{Mg(H}_2\text{O)}_6][\text{Sb(OH)}_6]_2$	trigonal	(35)
$[\text{Mg(H}_2\text{O)}_6][\text{Sb(OH)}_6]_2$	triclinic pseudomonoclinic	(35)
$[\text{Co(H}_2\text{O)}_6][\text{Sb(OH)}_6]_2$	triclinic pseudomonoclinic	(35)
NaSbF_6	rhombohedral	(9)
KSbF_6	cubic	(8)
RbSbF_6	rhombohedral	(11)
CeSbF_6	rhombohedral	(11)
NH_4SbF_6	rhombohedral	(11)
AgSbF_6	cubic	(36)
TlSbF_6	rhombohedral	(11)
$\text{NaSbF}_4(\text{OH})_2$	trigonal	(9)
$[\text{CH}_3)_2\text{NH}_2][\text{SbCl}_6]$	orthorhombic	(37)
$[\text{CH}_3)_4\text{N}][\text{SbCl}_6]$	cubic	(37)

within octahedra are not all the same, a situation that could not arise if the octahedra were perfectly regular. Using the distances of Schrewelius, a configuration could not be obtained that met the requirements of all Sb-F bonds having an interatomic distance of 1.95 \AA . Teufer (10) later placed the Sb-F distance at 1.78 \AA , which agreed with the distance in KSbF_6 found by Bode and Voss (8). Additional data found by the latter two authors are: F-F distance within octahedra, 2.38 and 2.60 ; F-F distance between octahedra, 2.74 ; and K-F distance, 2.74 \AA . They also suggested that the sum of the ionic radii would give an Sb-F distance of 1.95 \AA .

X-ray analyses on other compounds also led to reports of irregular octahedra, regardless of the cation. For example, Schrewelius (11) reports distortions of the octahedral anions in CsSbF_6 , RbSbF_6 , NH_4SbF_6 , and RbSbF_6 in addition to distortions of the CsCl type lattice to resemble that of the BaSiF_6 (12) lattice.

A perfectly regular octahedral complex can be slightly distorted to fit the data of Bode and Voss by performing two similar operations which consist of the convergence of three of the fluoro ligands along a sphere of radius 1.78 \AA to give six short and six long F-F distances, an arrangement that is appealing because of its symmetry. The coulombic attraction between the cation and the electron centers of the distorted anion would account for the reduction of symmetry of the crystal lattice, i.e., in the case of KSbF_6 , the eight nearest neighbors of any potassium ion would orient their axes in different directions.

There is some evidence that Sb(V) may expand its coordination to seven with fluoride. Marignac (13) obtained the hydrated heptafluoroantimonates of potassium and ammonium by adding an excess of KF or NH_4HF_2 to an HF solution of the antimonate. $\text{K}_2\text{SbF}_7 \cdot 2\text{H}_2\text{O}$ is described as possessing bright beautiful crystals that are preserved well in air unless the air is very humid. At 90°C it dissolves in its water of crystallization, then resolidifies, losing both H_2O and HF, to a product that does not completely dissolve in water. Other salts containing seven fluoride atoms are $\text{K}_2\text{SbF}_7 \cdot \text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SbF}_7 \cdot 1/2 \text{H}_2\text{O}$ and (quinine $\cdot \text{H}$) $_2 \text{SbF}_7$ (14). The structures of these salts are unknown and therefore it is not certain that the antimony has coordination number seven.

Studies of heptachloroantimonate salts have provided evidence that Sb(V) is not seven coordinate. The salts MgSbCl_7 , FeSbCl_8 and CrSbCl_8 are known, but they can be shown to contain the SbCl_6^- ion and can best be written as ClMgSbCl_6 , $\text{Cl}_2\text{FeSbCl}_6$ and $\text{Cl}_2\text{CrSbCl}_6$ (14) since AgNO_3 will precipitate one chloride, two chlorides and two chlorides respectively.

Structures in the Liquid State.--Evidence about the nature of the ions in solution is less definite than in the solid state, but all of the evidence supports the view that the antimony(V) is six-coordinate and octahedral. The best piece of evidence arises from the Raman spectra work on SbCl_6^- by Redlich (15, 16). Brintzinger (17) presents evidence for $\text{Sb}(\text{OH})_6^-$ from dialysis experiments, but the validity of his methods has been questioned by Souchay (18). Nevertheless Souchay and

Peschanski (19) from light absorption measurements, agree that $\text{Sb}(\text{OH})_6^-$ is the predominant Sb(V) species at high pH.

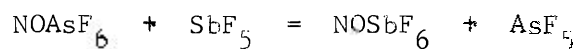
Hoffman, Holder, and Jolly (20) studied the nuclear magnetic resonance moments of liquid SbF_5 , and suggested that SbF_5 consists of long chains of octahedral SbF_6 groups, each group sharing two of its fluorine atoms with two neighbors. They also suggested that there are three groups of fluorine atoms, each possessing different ionic character.

SbF_5 and the Hexafluoroantimonates. --The alkali and ammonium fluoro salts can be prepared by adding alkali or ammonium hydroxide to an HF solution of SbF_5 (21). Although the preparation appears simple, and indeed it can be, there are inherent difficulties which arise when evaporating a solution that contains SbF_5 in HF. For this reason a brief review of the chemistry of SbF_5 is included here.

Mellor (22) presents an excellent review of the early work performed with SbF_5 and its salts. Although the cleanest method, undoubtedly, is the direct union of the elements, the drawbacks to this method are obvious. From Mellor's review it can be ascertained that early attempts to prepare SbF_5 by evaporating a solution of Sb_2O_5 in HF were unsuccessful until Marignac evaporated the solution in vacuo to obtain a gummy mass. Ruff and Plato (23) prepared SbF_5 by boiling at 25-30°C a mixture of HF and SbF_3 saturated with chlorine, distilling off the HF, and then collecting the SbF_5 at its boiling point, which they reported as 150°C. Ruff (24), investigating the compound further, noticed unexpectedly large amounts of SbF_5 at 100°C and therefore,

suspected an azeotrope. Shair and Schurig (25), who studied the vapor-liquid equilibrium of SbF_5 in HF, prepared SbF_5 via Perkins and Irwin's method (26), i.e., they bubbled excess HF into SbCl_5 . Shair and Schurig found mixtures of $\text{SbF}_5 \cdot x\text{HF}$ ($x = 0-5$) but no azeotrope, in a non-ideal system. One might expect that since the boiling points of the two liquids are vastly different (SbF_5 boils at 142.7°C ; HF at 19.4°C), HF would be almost completely evaporated before SbF_5 would exert any vapor pressure, however there is appreciable SbF_5 in the vapor (approx. 9.0 per cent) when the liquid contains 50 mole per cent of each. They attributed the nonideality to the disparity in the size of the molecules, the formation of an $\text{SbF}_5 \cdot 5\text{HF}$ solvate below 70°C , the association of HF molecules and hydrogen bonding between HF and SbF_5 .

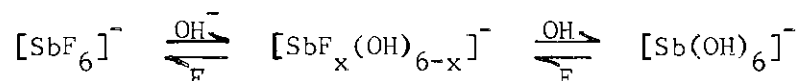
The acid strength of SbF_5 was demonstrated by Clifford, Beachell, and Jack (27), who observed that SbF_5 was the strongest acid among the twenty-odd fluorides they investigated. Their demonstration consisted of determining the solubility of the fluorides in HF (SbF_5 dissolved exothermally), observing the ability of the HF solution to dissolve various metals and then classifying the fluorides as to acid strength. This fact can be used to advantage in preparing some of the salts of SbF_6^- , i.e., SbF_5 can react with the salt of a weaker acid. For example, Ruff (28) prepared NOSbF_6 by warming NOAsF_6 with SbF_5 .



The alkali hexafluoroantimonate can be prepared by heating NOSbF_6 with the metal fluoride (29).

Woolf and Emeleus (29) used a fluorinating agent, BrF_3 to interact with the metal halide and Sb_2O_3 to prepare their salts.

Qualitative Features of Hydrolysis.--Armed with the evidence that Sb(V) is six-coordinate, we proceed to the preliminary discussion of the hydrolysis reaction. Lange and Askitopoulos (30) dissolved various alkali salts of HSbF_6 in water and found that the solutions were acidic; therefore, they concluded that hydrolysis took place and that the system would be expected to react according to the following scheme:



The reported intermediate products of the hydrolysis reaction vary, depending on environment and time of analysis. Some information on the intermediates is available from preparative work reported in the literature.

Thus Marignac (31) reported a salt resulting from the hydrolysis of NaSbF_6 had to have the formula $\text{NaF.SbOF}_3 \cdot \text{H}_2\text{O}$, or in modern notation, $\text{NaSbF}_4(\text{OH})_2$. However, Kolditz and Rehak (32), analyzing a salt prepared by Marignac's method identified it as NaSbF_5OH . Similarly the $\text{CsF.SbF}_4(\text{OH})$ described by Wells and Metzger (33) was identified as CsSbF_6 . The apparent discrepancies may in part be due to disregard of the time allowed for hydrolysis in otherwise identical preparative procedures.

In the experiments to be reported in this thesis there is a

difference in the nature of the starting species, beyond the fact that SbCl_6^- is the complex in one case, and SbF_6^- the complex in the other. Because of the thermodynamic instability of SbCl_6^- in solutions of low Cl^- concentration, and because the concentration of SbCl_6^- can be determined spectrophotometrically, the SbCl_6^- can be introduced into the reaction from a stock solution of Sb(V) in concentrated HCl. The species undergoing reaction is then the octahedral complex SbCl_6^- , as it exists in solution. Since SbF_6^- does not absorb ultra-violet radiation as does SbCl_6^- , the spectrophotometric method possible with the latter cannot be used with the former. The rate of reaction of SbF_6^- is followed by titration of the released fluoride ion. This method does not permit the introduction of SbF_6^- from a stock solution in HF, but requires that it be introduced as a solid salt. Hence the initial reaction may be that of SbF_6^- as it dissolves from the lattice. It is for this reason that some attention has been given in the previous discussion to the crystal structures of the solid state hexafluoroantimonates, while discussion of the corresponding hexachloroantimonates has been omitted.

CHAPTER II

EXPERIMENTAL

Preparation of KSbF_6 and NaSbF_6

The preparation of the fluoride salts for the hydrolysis experiment is basically that of Marignac (21). Solution of the proper antimonate in HF and evaporation of the ensuing solution produces the hexafluoroantimonate. SbF_6^- is present only if the solvent contains 40 per cent or more HF. If there is less than 40 per cent HF, the salt will be a hydroxo-halo compound. Marignac (13) describes KSbF_6 as non-deliquescent and NaSbF_6 as deliquescent.

An early attempt to prepare KSbF_6 by oxidation of an HF solution of Sb_2O_3 and KF with H_2O_2 resulted in a product that contained 4.2 per cent Sb(III). Another experiment followed: Sb_2O_3 was dissolved in KOH (approximately 6 N.) and treated with H_2O_2 ; the reaction proceeded vigorously. A beaker inverted over the reaction vessel collected a white powdery solid while standing over night. Qualitative analysis showed that antimony was present in this solid. Antimonate was recovered from the reaction vessel and treated with HF to give KSbF_6 . The yield was poor, and the product contained some Sb(III).

The procedure finally adopted was the following: 0.05 mole of Sb_2O_3 was mixed with 0.11 mole (10% excess) of solid KOH, and H_2O_2 was added slowly, a few ml. at a time. The very vigorous and exothermic reaction was carried out in a glass beaker as it blistered

one made from polyethylene.

During the reaction the initial powdery Sb_2O_3 was converted to a porous, more calcined, solid. H_2O_2 treatment continued until reaction was no longer prevalent, whereupon 10 ml. more of H_2O_2 was added and the mixture left standing for at least three hours. The liquid was decanted off and with it disappeared any excess of the potassium ions. The remaining solid was transferred to a polyethylene beaker and to it was added 65 ml. of 48 per cent HF. After heating on a steam bath under a hood for 30 minutes most of the solid dissolved; however, there remained a slight yellowish residue (possibly Sb_2O_5) which was filtered off. The clear solution was evaporated to a volume of 20 ml. and cooled. A white crystalline substance appeared. This was recrystallized twice from 48 per cent HF, dried on filter paper and placed in a polyethylene beaker within a desiccator. In addition to CaCl_2 and silica gel the desiccator contained solid NaOH to neutralize any HF present as the salt still had the odor of HF clinging to it. The NaOH pellets were replaced after each treatment of the salt with HF. Analysis of the salt showed

	Calculated %	Found %	Avg.
Sb	44.30	43.02, 43.04	43.03
F	41.50	41.69, 42.29	41.99
Ratio F/Sb	6.0		6.3

After three days in the desiccator, the salt no longer possessed the odor of HF and dissolved rapidly in water, HCl or NaOH solution. In about three weeks the KSbF_6 became difficult to

dissolve in water or acid and slightly less difficult to dissolve in base. Analysis of the salt then showed:

	Calculated %	Found %	Avg.
Sb	44.30	44.10, 44.01	44.05
F	41.50	40.26, 41.48	40.87
Ratio Sb/F	6.0		5.9

Recrystallization of this salt from HF caused it to again dissolve readily in water or acid. Heating on the steam bath for fifteen minutes made the salt difficult to dissolve. After recrystallization from HF, drying on filter paper and placement in the desiccator for three days, the salt readily dissolved in H_2O .

By "difficult to dissolve" is meant that all of the salt does not dissolve immediately. A good portion of it surely does; however, the rest may go into solution only after vigorous shaking for as long as fifteen minutes, or it may not go in at all, even after heating. Disregarding all other aging factors, two factors would appear to influence the ease of solution. The first would be that it depends on a slight excess of HF which would likely cling to the crystal surface and the second, more plausible one, is that over a period of time, either by repeated exposure to the atmosphere or by reaction with a very minute amount of water vapor in the desiccator the $KSbF_6$ picks up enough water to form some Sb-O-Sb bonds.

Antimony in some form was lost during the evaporation of the HF- $KSb(OH)_6$ solution. This was most evident from the formation on the window of the hood of a solid which contained antimony. Upon

preparing NaSbF_6 , using the same method as for KSbF_6 , the solid deposited on the window more profusely. The loss of antimony may be attributed to the volatilization of either SbF_5 or $\text{SbF}_5 \cdot x\text{HF}$. Shair and Schurig list the vapor pressure of SbF_5 at 106.1°C as 216.9 mm. Hg. In solution with HF and H_2O , there is little to be gained from this value except that SbF_5 could exert a slight vapor pressure which, over a period of hours on the steam bath, could account for the loss of antimony.

The recovery of NaSbF_6 was small compared to KSbF_6 and after storage in the desiccator for a period of a week it was found that the sodium salt reacted with the water vapor in the air very slowly. The potassium salt is not so deliquescent; however, it will gain weight if permitted to remain exposed to the atmosphere over prolonged periods. More precisely, the salt's gain in weight was 0.1 per cent over a period of three hours.

One further result was observed. The sodium salt, which was crystal clear when placed in the desiccator, had an estimated 25 per cent conversion to a black material. The polyethylene beaker, which contained the crystals, turned coal black and had an odor of caramel. The potassium salt, which was white, possessed a grayish tint after storage and also had a faint caramel odor, in one of the several preparations. In both cases the dark material dissolved readily.

Analytical Methods

Analytical procedures were necessary for the following purposes:

- (1) Determination of the composition of isolated compounds as a

means of verification of their identity, and (2) determination of the concentration of free fluoride ion during the hydrolysis of SbF_6^- .

Analysis for Fluoride in Isolated Compounds.--The fluorine was first volatilized as fluosilicic acid, using Armstrong's modification (38) of the method of Willard and Winter (39). Steam was passed through the solution of the compound in HClO_4 rather than using the dropping funnel as suggested by Willard and Winter. In order to give more precise results it became necessary to perform the titration in an aqueous medium adopting another modification by Armstrong (40) which was found by Rowley and Churchill (41) to give a definite end point when between one and fifty mg. of fluorine is present. A buffered solution is essential and is prepared from sodium hydroxide and chloroacetic acid following the instructions of Charlot and Bezier (42).

The actual procedure is described in the following paragraph. To a weighed sample of KSbF_6 in a volumetric flask is added distilled water up to the mark. A 5.0 ml. aliquot is transferred to a distilling pot that contains 10 ml. of H_2O , 15 ml. of concentrated HClO_4 , and pieces of broken glass, all at a temperature of 135°C . Two 60 ml. portions of distillate are collected in separate 125 ml. Erlenmeyer flasks. To these are added six drops of 0.05 per cent aqueous sodium alizarin sulfonate solution as indicator. Dilute HCl or NaOH is added until the pink color of the indicator disappears. Then 2.5 ml. of buffer solution is added. The fluoride is titrated with a $\text{Th}(\text{NO}_3)_4$ solution which is approximately 0.011N, until the pink color matches that of a blank. Since the pink color of the blank increases in intensity upon standing fresh solutions were prepared frequently.

Analysis for Antimony in Isolated Compounds.--Analysis for antimony (III) was necessary to determine the amount of Sb(III) that was not oxidized to Sb(V) in the preparation of the hexafluoroantimonate from Sb_2O_3 . The method used was that of Fales and Kenny (43), involving titration with I_2 in neutral solution. A weighed sample of salt was dissolved in water. After heating, three g. of tartaric acid in five ml. of water was added, and the heating of the solution was continued for five minutes more. Thereafter, the solution was cooled, diluted with fifty ml. of distilled water, neutralized with NH_4OH , treated with five grams of sodium bicarbonate and titrated with a standard iodine solution to an end point enhanced by the addition of three ml. of 1% starch solution.

The method attempted for determination of antimony (V) was basically that described by Willard and Diehl (44), in which Sb(V) oxidizes iodide in strong acid, and the liberated iodine is titrated with thiosulfate. The KSbF_6 is dissolved in enough concentrated HCl to maintain a concentration in the vicinity of 3 M at the end of the titration. One gram of sodium bicarbonate, added in four portions, creates a carbon dioxide atmosphere. This step is followed immediately by the addition of one gram of potassium iodide in three ml. of distilled water. The flask is then stoppered to prevent air oxidation of iodide. The resulting solution is titrated with a standard $\text{Na}_2\text{S}_2\text{O}_3$ solution to the disappearance of the iodine-starch blue color.

Although the method gives satisfactory results for solutions prepared from antimony pentachloride, complications arise when the solution is prepared from KSbF_6 , or when fluoride ion is present. The

observed end point always gives a low value for antimony and is not reproducible. On further standing of a titrated solution in a carbon dioxide atmosphere, the deep blue color of the starch complex returns indicating that more iodine is being formed. Comparison with a blank demonstrated that this increase could not be attributed to air oxidation.

This suggested that SbF_6^- and/or other fluo-complexes did not oxidize iodide to iodine, either for thermodynamic or kinetic reasons. Three sets of experiments were performed to gain more information on the interference by fluoride ion, and to find means of eliminating the interference. In each set of tests a solution containing Sb(V) in concentrated HCl was prepared and titrated by the procedure already described. (The antimony came from stock solutions of antimony pentachloride in concentrated HCl.) Since there is no interference under these conditions this titration is taken to be a measure of the amount of antimony present. In other tests additional substances were added in the sequence listed before beginning the titration. Unless time intervals between additions are specified the substances are added one after another at normal working speed. Some of the results are as follows:

Test No.	Solution Titrated	mls. $\text{S}_2\text{O}_3^{=}$	% Deviation
1a	10 ml. stock solution I		
	3 ml. concentrated HCl	34.20	---
1b	Same as 1a, plus 2.5		
	grams tartaric acid	34.18	---

1c	Same as 1a, plus 0.30		
	grams of NH_4HF_2	30.30	11.14
1d	Same as 1a, plus 2.5		
	grams tartaric acid, 0.30		
	grams NH_4HF_2	27.58	19.4
1e	5 ml. of stock solution II		
	6 ml. concentrated HCl		
	0.15 grams of NH_4HF_2 , 15 ml.		
	of 1.0 M AlCl_3	15.68	8.3
2a	5 ml. of stock solution II		
	3 ml. of concentrated HCl	24.90	---
2b	Same as 2a	24.85	---
2c	Same as 2a, plus 1 gram		
	CaCl_2 in 5 ml. H_2O	24.90	---
2d	Same as 2c	24.90	---
2e	Same as 2a, plus 0.25 gram		
	NH_4HF_2 , 1 gram CaCl_2 in 5 ml.		
	H_2O	11.30	54.6
2f	Same as 2e	10.95	56.1
2g	Same as 2e, but heated on a		
	steam bath for one hour		
	before titrating	15.67	37.0
2h	Same as 2a, plus 0.25 gram		
	NH_4HF_2 , 3 grams CaCl_2 in 5 ml.		
	H_2O ; allowed to stand 2 days	21.42	13.8
	After 6 hours more	23.02	

3a	5 ml. of stock solution III		
	3 ml. concentrated HCl	25.07	---
3b	Same as 3a, plus		
	1 gram H_3BO_3 in 5 ml. H_2O	25.02	---
3c	Same as 3b	24.83	1.0
3d	Same as 3a, plus		
	0.25 gram NH_4HF_2		
	Allowed to stand 2 hours before		
	titrating	19.68	21.6
3e	Same as 3d, but 1 gram of		
	H_3BO_3 in 5 ml. of H_2O added after		
	the 2 hours of standing	23.98	4.3
3f	Same as 3e, but the solution was		
	heated just below boiling for		
	5 min. after addition of		
	H_3BO_3	24.68	1.6
3g	Same as 3f	25.06	0.0

The above sampling of experiments indicates that the addition of H_3BO_3 followed by heating should prove a very satisfactory method of titrating quinquevalent antimony in the presence of fluoride ion. The percentage error in this method is normally less than two per cent.

In addition, the above experiments give some indication of the process that is taking place. Evidently the fluoride ion complexes with the quinquevalent antimony. As the fluoride is released by the

antimony it may be bound to any other substance which complexes with fluoride. The extent to which the total fluoride is distributed between antimony and the competing reagent will be determined by the complexing constants. The success of H_3BO_3 in accomplishing the total removal of fluoride from the Sb(V) is apparently due to the greater stability of the fluo-complexes of boron.

Determination of Fluoride During Hydrolysis.--The original titrations for fluoride ion were performed by transferring a 5 ml. aliquot (4 ml. for solution that contained more than 0.6 N HClO_4) to a 125 ml. Erlenmeyer flask, adding 20 ml. of 95 per cent ethyl alcohol, indicator, buffer, enough distilled water to maintain a volume of 50 ml. at the end of the titration, and titrating with $\text{Th(NO}_3)_4$.

This method gives a well-defined end point if the volume of titrant is held below about ten ml. If more than this amount is needed the end point becomes difficult to determine because the solution appears turbid and the intensity of the pink color does not seem to be sensitive enough to the addition of more $\text{Th(NO}_3)_4$ solution. The limit of 10 ml. of titrant will allow adequate studies of the hydrolysis only for the replacement of the first and second fluorides. For fluoride titration in the analysis of continued hydrolysis an aqueous medium is necessary. In solutions that contained greater than 0.8 M HClO_4 before dilution it was necessary to add four ml. of buffer to make the final pH of the solution fall in the range 2.9 to 3.1 as determined by a Beckman pH meter.

The advantage of the aqueous method of titration is a more definite end point especially when determining large values of fluoride.

The insolubility of ThF_4 in alcohol makes the solution too turbid to see the end point clearly. The disadvantage of the aqueous method is the difficulty in maintaining the pH of the solution within the essential limits, particularly when the solution contains high concentrations of perchlorate ion. A pH of 2.7 at the end point was found to require up to one ml. more titrant than was required between pH 2.9 and 3.1. The aqueous method was used from the eleventh run on.

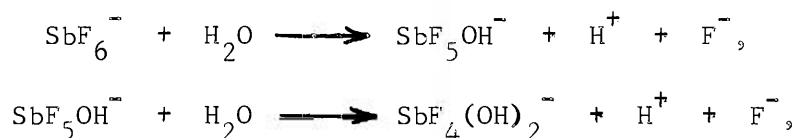
Perchloric acid does not interfere appreciably with the titration of 0.003 M fluoride if the perchlorate concentration is less than 0.1 M (45). The hydrolysis run in the lowest pH range was made in concentrations of perchlorate ion that were close to this value and it is possible that the perchloric acid interfered with the titration. Perchlorate ion gives a high value of fluoride.

An attempt is made in this work to adopt a standard method of adding the titrant; therefore, the titrant is added rapidly but dropwise until the volume used approaches within one ml. of the end point, then the titrant is added at ten drops per minute.

CHAPTER III

HYDROLYSIS OF SbF_6^-

The evidence cited in Chapter I strongly suggests that hydrolysis of SbF_6^- proceeds in step-wise fashion by reactions of the type



etc. In solution the hexafluoroantimonate ion forms free fluoride ion upon standing, and it is expected that titration of this free fluoride will give the rates of hydrolysis. Therein lies the general attack on the problem. Furthermore, the replacement of a fluoride ion with a hydroxide ion yields a hydronium ion which can be titrated. Because of their nature our experiments do not identify the other products of the hydrolysis. For this we must rely on the work of previous investigators, and particularly on Kolditz and Sarrach (46).

Experimental.--The salt KSbF_6 was used as the source of SbF_6^- ions. The reaction was begun by dissolving a weighed portion of the salt in a solution of the desired composition. The time required for dissolution varied with the age of the salt and the nature of the solution, and was of the order of several minutes. The recorded starting time for hydrolysis was the time of the first addition of solution to the salt in a volumetric flask. The flask was then thermostated at 25°C ,

and aliquots removed at appropriate intervals for analysis. A titration for free fluoride ions was made as soon as possible after solution of KSbF_6 and was followed by a titration for hydronium ion when feasible. The time intervals for subsequent titrations varied depending on the speed of reaction. For fast reactions titrations were made frequently until the reaction slowed down, and for slow reactions approximately five additional titrations were performed on the first day of hydrolysis, three on the second day, and one or two on the following days.

The fluoride ion was titrated with standard thorium nitrate as described in Chapter II. The hydronium ion was titrated with standard sodium hydroxide. The end point was determined potentiometrically with a Beckman Zeromatic pH meter.

The rate of hydrolysis was determined in solutions which were 0.01094 M in KSbF_6 , and were of varying pH. In the acidic region perchloric acid was chosen since the perchlorate ion would not be expected to complex with Sb(V). The extremes of acidity or basicity were 1.0 M in NaOH and 1.172 M in HClO_4 .

Results of Fluoride Titration--In acid or neutral solution the stepwise replacement of fluoride by hydroxide ion can be observed. When the free fluoride ion concentration, after subtraction of an equilibrium value, is plotted vs. time, fairly distinct breaks are observed for the replacement of one, two, and four fluoride ions. In no case is replacement of more than four fluorides observed, even after periods as long as four months. It is not clear whether this results from a thermodynamic or kinetic limitation. Furthermore, polymer

formation increases the complexity of the system at this stage.

To indicate the general trend of the reaction a plot of $\log W$ vs. time is made, where W is the per cent of fluoride remaining complexed. Several such plots are shown in Figure 1. The total fluoride content is calculated from the weight of KSbF_6 . The concentration of free fluoride is found from the fluoride titration, and by comparing its value to the total fluoride, the per cent fluoride remaining complexed is calculated. For the sake of clarity some of the points near the origin are omitted. Most of the runs are continued to times greater than that shown, and the curves eventually approach one another with approximately the same percentage of fluoride remaining on the antimony. The run in which KSbF_6 is dissolved in H_2O is shown in Figure 2 to illustrate the difference in the data between the fluoride titration and the acid titration.

Evidence for the immediate removal of the first fluoride is abundant. The titration of fluoride never gave a value above 82 per cent F^- remaining, and although the earliest readings were taken seven minutes after the addition of solution to solid KSbF_6 , extrapolation to zero time shows about one-sixth of the fluoride replaced. Since the titration is performed in a buffered medium of pH 2.9 - 3.1, it may be argued that the hydrolysis of the first fluoride occurs in this buffer during the titration rather than prior to it. To check the behavior in the absence of the buffer 0.416 gram of KSbF_6 was dissolved in 100 ml. of distilled water and the pH was determined within a minute to be 2.60 (a Beckman Zeromatic pH meter was used). Using 6.9×10^{-4} as the ionization constant of HF, the

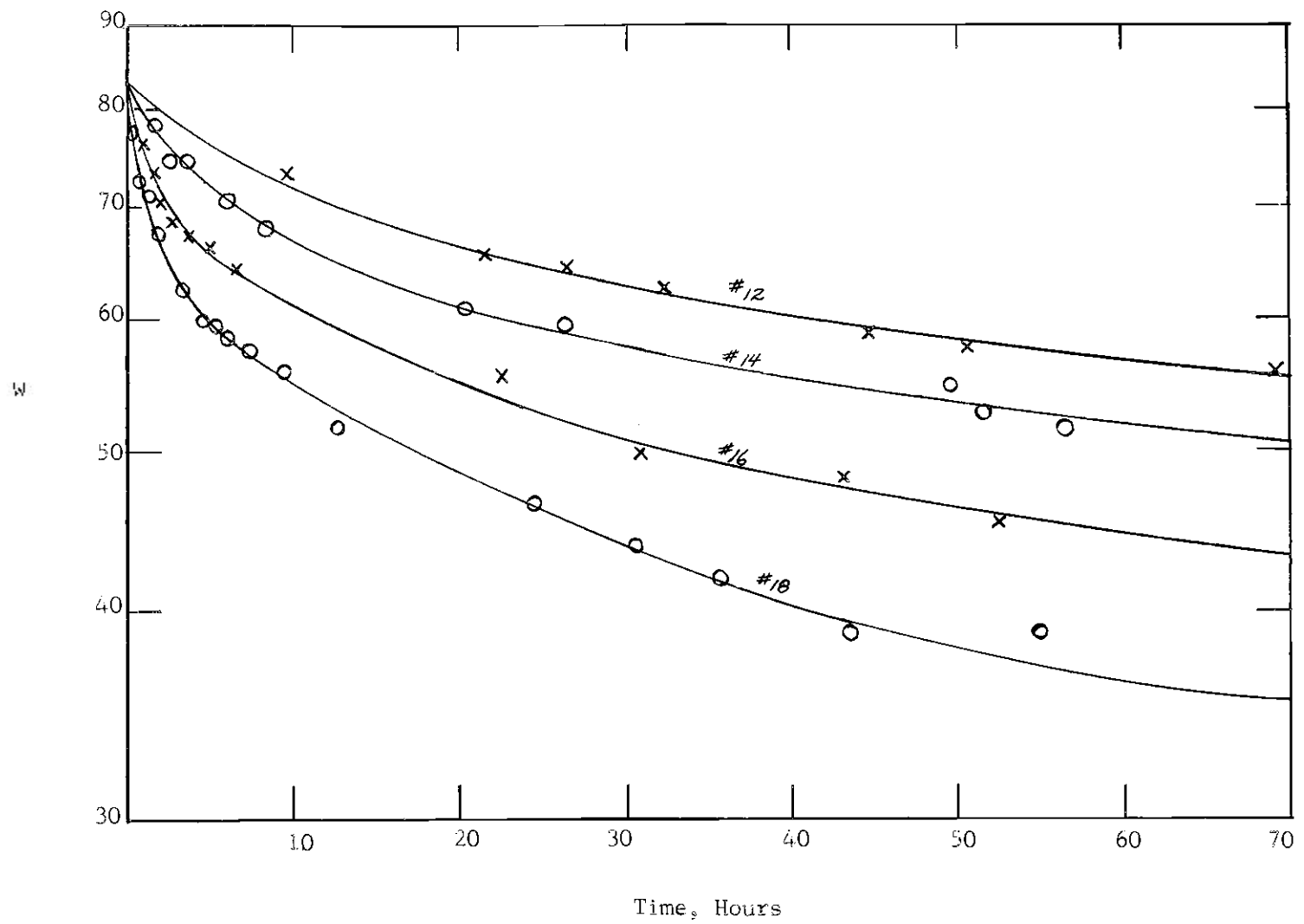


Figure 1. Plot of Log W vs. Time (Runs 12, 14, 16 and 18).

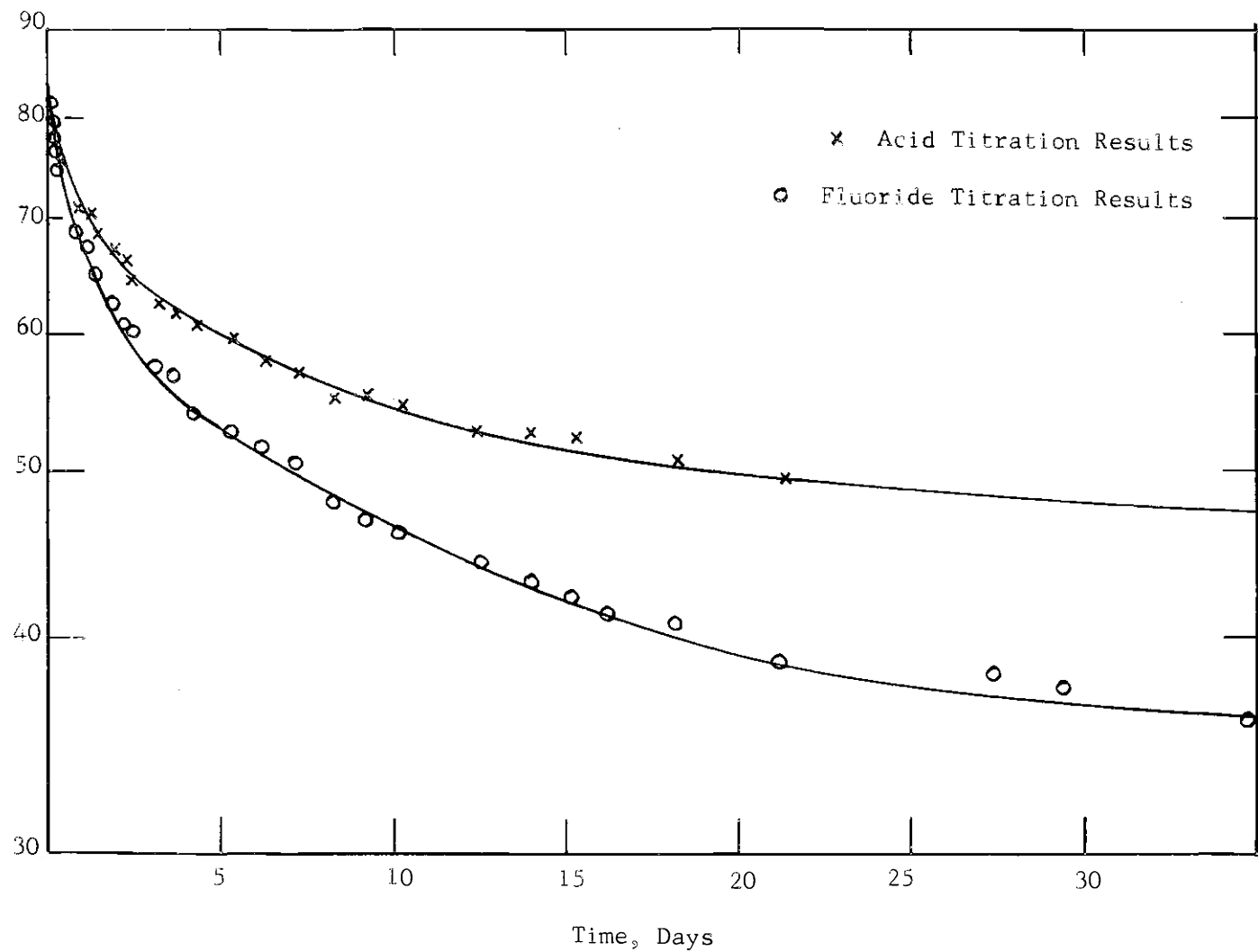


Figure 2. Plot of Log W vs. Time. Calculated from Acid Titration and from Fluoride Titration. (Run No. 11).

calculated pH value is 2.56 for replacement of the first fluoride. Our results concur with those of Kolditz and Sarrach (46) who concluded that SbF_5OH^- was practically the only species in solution at this point of the hydrolysis reaction.

Treatment of Data.--The simplest assumption to be made is that the system consists of several consecutive first order or pseudo-first order reactions. If this is the case it should be possible to resolve each of the curves in Figures 1 and 2 into its straight line components.

When it became manifest all of the fluoride would not be replaced in acidic solution, it was decided that perhaps the hydrolysis reaction would be completed after two-thirds of the fluoride was replaced since the reaction became extremely slow in the area of 60 per cent replaced and 66.7 per cent replaced is the value that represents the replacement of an integral number of fluorides.

A plot of $\log (W-33)$ vs time was made but the graphs did not give good resolution as the plotting of a straight line was difficult. Also the intercepts at the zero time axis were not at 50, 66.7 or 83.3 per cent fluoride remaining. These intercepts would be reasonable if the rate of hydrolysis would change after the replacement of an integral number of fluorides per antimony atom. Among the reasons for failure were considered the following (1) the HF in solution attacked the silicate in the glass volumetric flasks, (2) the solid which formed during the runs and about which more will be written later trapped or carried some fluoride with it and (3) an equilibrium was established.

The first consideration would not likely interfere because the attack of silicate by HF would form H_2SiF_6 which is exactly the form of the fluoride in the first analytical method described in Chapter II. Any contribution to error by the solid that formed was alleviated by swirling the solution before taking an aliquot in order to get a representative sample. The third consideration presents a method of attack that can best help to resolve the data.

Some of the runs were followed for months, others were heated to speed up the reaction in order to obtain an infinite time reading. Values obtained were 64.45, 65.11, 64.35, 65.60 and 64.92 per cent fluoride replaced. 35.00 per cent fluoride remaining was chosen as the equilibrium point of the reaction since the choice of a round number greatly facilitates the hundreds of calculations that are necessary. While a difference of 1.67 per cent may not appear to be a great deal, the results were gratifying.

First a plot was made of $\log 2 (W-35)$ vs. time. A factor of two was incorporated to give better resolution on semi-log paper. Such a plot is shown in Figure 3. Some of the runs (the ones in distilled water and 1.17 M HClO_4) gave much better plots but it would not be fair to call these typical runs nor would they give a fair indication to the method of plotting; therefore, let us say that the run shown is a typical run. The points are plotted and then a two per cent error in titration is assumed, i.e., if 10.00 ml. of titrant is used, then it is assumed that the correct value is 10.00 ± 0.20 ml. If 29.50 ml. of titrant is required for complete titration of all the fluoride, the value of the plotted point would

be $\log 2 \left[65.00 - \frac{10.00 \pm 0.20}{29.50} \times 100 \right] = \log 2 (65.00 - 33.95 \pm 0.60).$

The point $\log 2 (31.05) = \log 62.10$ is plotted and a vertical line 1.20 units in length is drawn on each side of the point or to facilitate plotting the line is drawn to the nearest horizontal line. If a straight line, through all of the vertical lines nearest the end of the run is not obtained, the per cent error is increased until a straight line can be drawn through all of the vertical lines. In this particular case a three per cent error is sufficient for the purpose. The half-time of hydrolysis is calculated from the slope of the line.

The range of the straight line indicates that the hydrolysis of the fourth fluoride can not be slower than the hydrolysis of the third fluoride and therefore both would appear to come off together. Kolditz and Sarrach (46) enlightened this phase of the reaction when they attempted to prepare $\text{KSbF}_3(\text{OH})_3^-$. Since they could prepare $\text{SbF}_5(\text{OH})^-$ by treating KSbF_6 with water, and $\text{SbF}_4(\text{OH})_2^-$ by mixing KSbF_6 and two equivalents of KOH , they expected to obtain $\text{SbF}_3(\text{OH})_3^-$ by mixing KSbF_6 with three equivalents of KOH . After mixing the ingredients and letting the mixture stand overnight they found $\text{SbF}_2(\text{OH})_4^-$ and some $\text{SbF}_4(\text{OH})_2^-$ but no $\text{SbF}_3(\text{OH})_3^-$. If the rate is slower after each removal of fluoride they should have been successful in preparing $\text{SbF}_3(\text{OH})_3^-$ and isolating the potassium salt before further hydrolysis. They succeeded in proving the existence of $\text{SbF}_3(\text{OH})_3^-$ by heating $\text{KSbF}_4(\text{OH})_2$ with one equivalent of KOH and analyzing soon after, but the greater part of the antimony was in the form of $\text{SbF}_2(\text{OH})_4^-$.

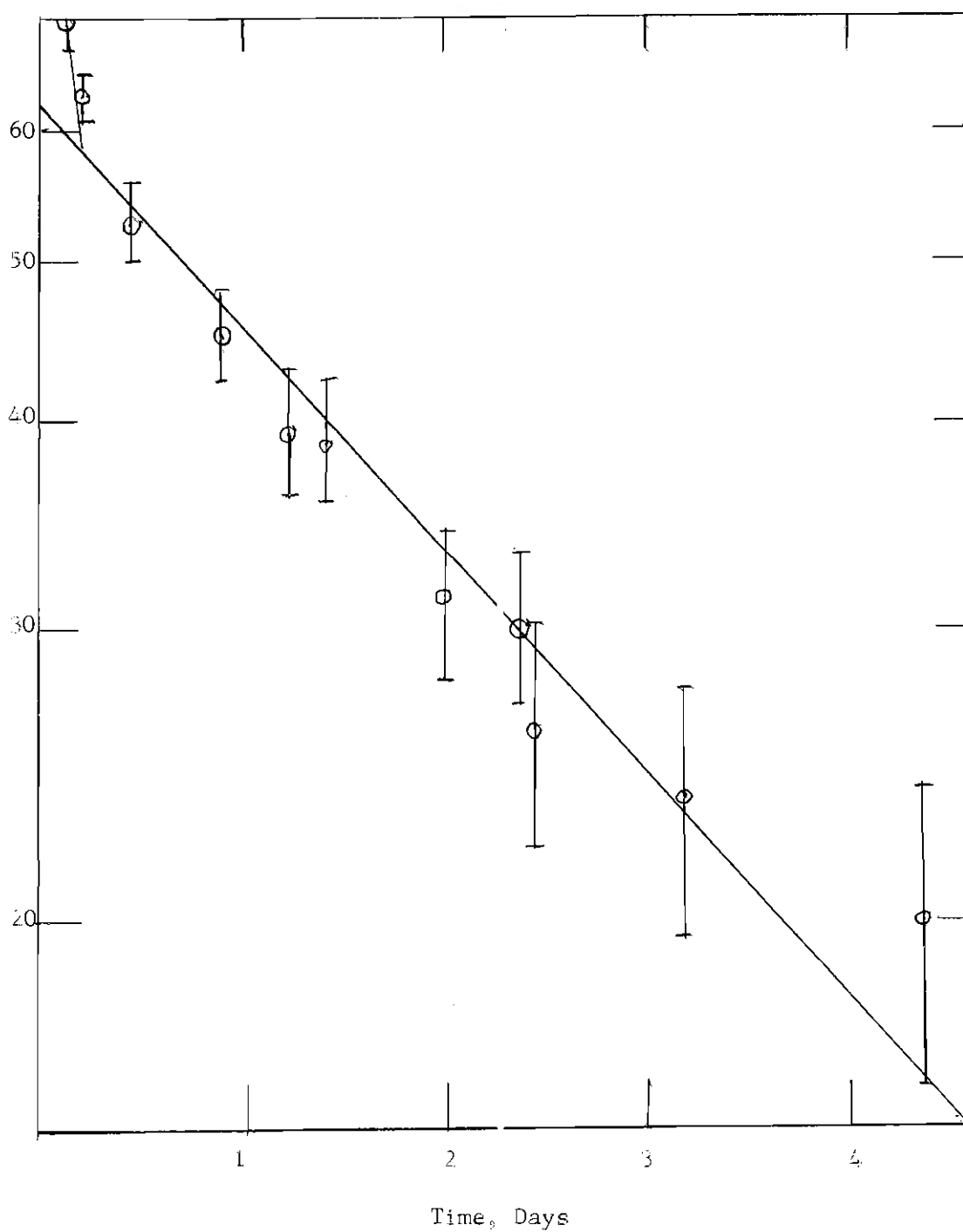


Figure 3. Plot showing slope from which $t_{1/2}$ is calculated for Third Step of Hydrolysis. (Run No. 15).

Since it is evident that the fourth step of the hydrolysis reaction is rapid in comparison to the third step, the two steps are considered as one and in an ideal situation the intercept at zero time should be $\log 2 (66.67 - 35.00) = 63.34$ per cent fluoride remaining. Table 2 lists the half-times and intercepts of some of the runs. Intercept A is the intercept for the third and fourth steps of the runs while $t_{1/2}(A)$ is the half-time for the third step. The half-time of the fourth step is unknown.

The half-time for the second step is calculated from the slope of the line obtained when the previous straight line is subtracted from the rest of the curve; the same basic procedure as before being followed. For greater resolution the values are doubled again and the actual point plotted is equal to $\log 4 (W - 1/2 \text{ value of the straight line})$. A one per cent error in titration during this step would give a vertical line that is twice as long as in the previous steps and an error of even five per cent would be devastating since such an error in titration would result in each point covering over 10 per cent of the vertical length of the graph. Fortunately, the accuracy of the titration is greatest in this region and an error of two per cent normally will fit in all of the data.

Figure 4 shows the plot of the resolved data for runs No. 15 and 16. Besides illustrating the method of resolution these two plots will also illustrate another phenomenon. The intercept for an ideal situation would be at $\log 4 (83.33 - 66.67) = \log 66.64$. The half-times and intercepts for the second step of the hydrolysis are listed in Table 2 as $t_{1/2} (B)$ and intercept (B) respectively.

Table 2

Results of Experiments with SbF_6^- (a)

Run No.	Solution (b)	$t_{1/2}$ (A)	Intercept A	$t_{1/2}$ (B)	Intercept B	S (c)
7	0.01100 <u>M</u> NaOH	5.8 days	64.4	-----	-----	-----
11	Distilled H_2O	6.7 days	61.8	15.8 hrs.	60.7	-----
12	0.01172 <u>M</u> HClO_4	5.9 days	61.3	13.2 hrs.	66.6	-----
13	0.08140 <u>M</u> HClO_4	5.2 days	58.6	9.2 hrs.	68.2	54.00
14	0.2096 <u>M</u> HClO_4	3.0 days	62.1	192 min.	65.1	-----
15	0.3985 <u>M</u> HClO_4	2.3 days	62.0	73 min.	95.2	45.60
16	0.6154 <u>M</u> HClO_4	29 hrs.	68.6	65 min.	58.8	31.40
17	0.8340 <u>M</u> HClO_4	18.5 hrs.	63.2	66 min.	85.0	34.00
18	1.076 <u>M</u> HClO_4	16.8 hrs.	61.0	60 min.	65.0	-----
6	0.09611 <u>M</u> NaOH	21 min.	-----	21 min.	-----	-----
5	0.9876 <u>M</u> NaOH	very rapid	-----	very rapid	-----	-----

(a) All solutions are 0.01084 M in KSbF_6 except 5 (0.1127 M) and 7 (0.1003 M).

(b) "Solution" designates composition of solution before addition of KSbF_6 .

(c) Column S is the per cent F^- released when solid was first observed. If no value is given then it was not recorded.

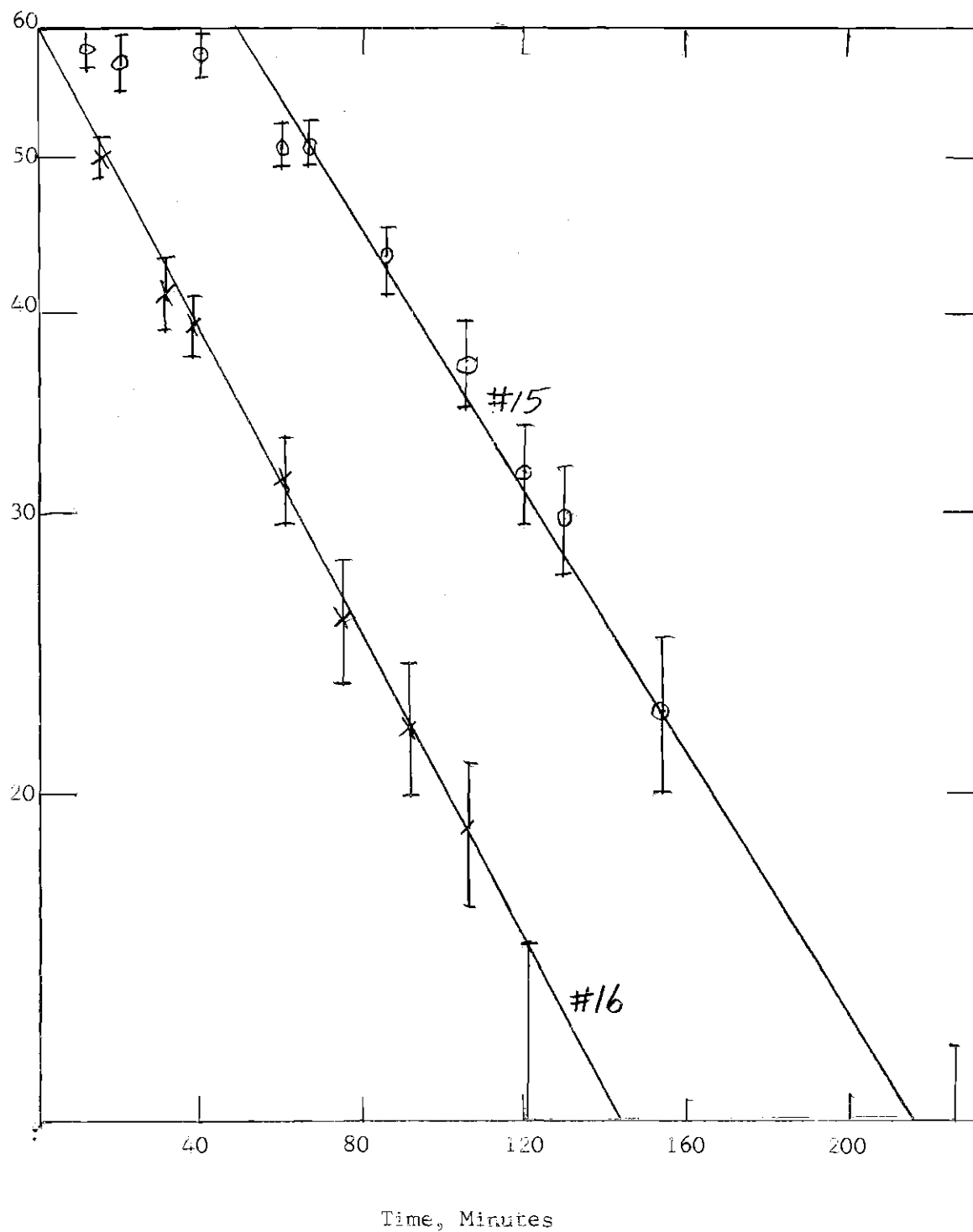


Figure 4. Plot showing slopes from which $t_{1/2}$ is calculated for Second Step of Hydrolysis. (Runs No. 15, 16).

It is seen that the intercept B in Run No. 15 is far removed from the expected value.

It was mentioned in Chapter II that upon standing KSbF_6 becomes more difficult to dissolve. Run No. 15 was a run in which KSbF_6 dissolved with difficulty and apparently the behavior near the intercept is a dissolution effect, i.e., although salt appeared to be completely dissolved before beginning the titration, it now appears to have passed through the colloidal state. The effective time of solution is other than the one recorded causing a large error in the intercept. This behavior can be eliminated by preparing a fresh batch of salt three to seven days before beginning a series of runs.

The reaction of all six steps in basic solution is extremely rapid and is complete in solution of pH 12 and higher. It may be complete in solutions of lower pH but in NH_4OH at pH 10.2 after a month of reaction 17 per cent fluoride still remained complexed. The reaction in 1.0N NaOH was so rapid that a fine white precipitate formed before the first aliquot was taken, while in 0.1N NaOH the rate was measurable and could be followed by both acid and fluoride titrations. The number of titrations are sparse because of the celerity of the reaction in base and only one half-time is given with no attempt to resolve the data.

Run No. 7 aids us in finding the pH range for the transition from fast to slow hydrolysis. The column reading "solution" in Table 2 designates the composition of the solution before addition of KSbF_6 . Of course, the acidity is greater than the ones listed and the increase

of acidity during a run might be expected to influence the reaction rates particularly in those solutions of low acid or base concentration. Although the influence is probably present, the acceleration or deceleration of rate is not great enough to become manifest during any particular run with the exception of Run No. 7. If we begin with 0.0110 N NaOH, the immediate replacement of the first F^- with OH^- neutralizes the base and for the beginning of the second step we have a neutral solution. The reaction continues rapidly until it begins to decelerate near the end of the second step (about pH 3.3) after which the reaction is normal and the prescribed method of resolution can be followed. Resolution does give a straight line for the third step but none can be obtained for the second step since the line is curved with an initial slope of 4.8 hours. From the data in Table 2 it can be seen that the hydrolysis increases with increasing acidity or basicity beyond a pH where the rate is at a minimum. The rate of hydrolysis for the third fluoride in Run No. 11 (pH 2.4 - 2.3) is slower than the rates in Runs No. 7 (pH 2.6 - 2.4) or 12 (pH 0.9); therefore, the minimum rate must be in the pH range of less than 2.4 and greater than 0.9. Of course, the minimum pH is for the third fluoride but since the rate of hydrolysis for the second fluoride begins to decelerate about pH 3.3 and increases with increasing acidity beyond pH 1, it can be assumed that both minimum pH's must be close to each other.

Accuracy of the Method.--The assumption of the same final equilibrium condition in all the solutions, even though of varied acid concentrations, is reasonable when one considers that product H^+ and F^-

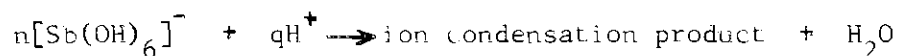
combine to form the weak acid HF. The intercepts can be altered by assuming a different equilibrium point than the one used. For instance, taking a value of 35.50 per cent fluoride remaining as the equilibrium point alters $T_{1/2}(A)$ by about 1-2 per cent and the intercept by about ± 0.8 units, bringing the average value close to the calculated 63.3 per cent. If we take an error of ± 4 per cent in titration to be the extreme limits of error for the third step and ± 2 per cent for the second step, varying the equilibrium point from 33.33 to 36.00 per cent F^- remaining and fit various straight lines to the extremes of the data, it is found that the values of the given half-times are accurate to ± 10 per cent.

Results of Acid Titration.---Attempts were made to follow the hydrolysis of SbF_6^- using the acid titration in Runs No. 7, 11, and 12, and by titrating with HCl in Run No. 6. Runs No. 6 and 11 gave satisfactory results, while Nos. 7 and 12 gave only mild success. In Run No. 11 it was observed that one hydronium ion was formed for each fluoride released until about 75 per cent fluoride remained. Thereafter, almost two fluorides are replaced per hydronium ion formed. All other runs showed the same result qualitatively, but were quantitatively less accurate because of the acidity or basicity of the solution before the addition of the salt. Although the possibility exists that some of the hydrogen ion formed in the hydrolysis is destroyed by reaction of HF with the glass, this explanation seems unlikely for two reasons: (1) the differences between the fluoride and acid titration appear at the same stage of the reaction in all cases,

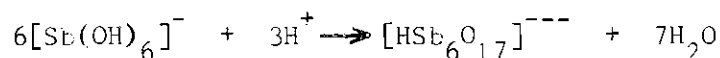
and (2) if the reaction with the glass is rapid enough to cause an effect within the first day one would expect a much greater effect than is observed after several months.

Assuming that the difference in the rate of fluoride release and rate of hydronium ion formation is due to the reaction of antimony species the system cannot be described solely in terms of the simple reactions so far presented. An interpretation, consistent with observations, is that polymerization of some kind occurs. Small particles of solid are observed to form during the reaction, and the stage of the reaction at which they were first observed is indicated in Table 2. The amount of total solid formed is only a small fraction of the antimony in solution.

Souchay and Peschanski (19) who studied the condensation reaction of $\text{Sb}(\text{OH})_6^-$, proposed an equilibrium of the type

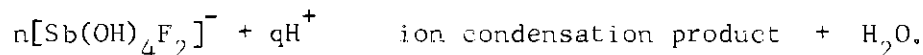


The reaction is fairly complete at a concentration of 1.2×10^{-2} M $\text{KSb}(\text{OH})_6$ and at a pH less than 2.5. From light absorption measurements they calculated n to be six and q to be 3 and the equation henceforth took the form:



There are 12 H_2O unaccounted for and because of the form of the equation it is likely that they are associated with the condensed ion so that the ion could be represented by the formula: $[\text{HSb}_6(\text{OH})_{24}\text{O}_5]^{---}$.

If we assume that a single analogous reaction occurs in the fluoro system the best choice is



It is assumed that (1) the condensation proceeds only after the formation of $\text{Sb}(\text{OH})_4\text{F}_2^-$, (2) the condensation reaction is rapid, (3) the condensation reaction goes to completion, and (4) there are two fluorides per antimony in the condensation product. If the reaction goes to completion the amount of fluoride retained at the end of hydrolysis would be independent of the concentration of acid.

Run No. 11 is the best run for determination of n/q since there are no complications of additional acid other than the acid from the hydrolysis reaction. Bearing in mind the assumption made, a measure of n/q can be calculated from the following ratio

$\frac{66.67 - x}{1/2(66.67 - y)}$, where x is the per cent hydronium ion released and y is the per cent fluoride released at the same time. The values must be taken in the region where it is certain that the first two steps of the hydrolysis reaction are complete in order to use the number 66.67.

The experimental ratios of n/q are 1.18, 1.17, 1.22, 1.19 and 1.11. If we consider possible values of n and q over the range of one to ten, the ratios $6/5$, $7/6$ and $8/7$ are found to be closest to the experimental value of 1.17. We can choose n as six in order to agree with Souchay and Peschanski; however, their experimental data indicates that n can also be seven. Since choice of a particular value of

n and q is not clearly resolved, we can argue only that the least number of complexed antimony ions involved in a condensation product is six. Moreover, q is numerically one less than n .

CHAPTER IV

Hydrolysis of SbCl_6^-

The hydrolysis of SbCl_6^- had previously been studied in acidic chloride solutions by Neumann and Ramette (2). At a total chloride concentration of 6 M the pseudo first-order rate constant was equal to $(3.9 + 0.8[\text{H}^+]) \times 10^{-3} \text{ min.}^{-1}$, and at a total chloride concentration of 9 M it was $(5.3 + 1.6[\text{H}^+]) \times 10^{-3} \text{ min.}^{-1}$. Thus the rate includes both a pH dependent and a pH independent term. Table 3 contains a list of half-times, compiled from results of previous experiments (47), for the reaction in HCl solutions. The reaction had not been studied in basic solution up to this time and the purpose of the present work is to extend our knowledge into this region.

Experimental.--Three Sb(V) stock solutions were prepared by transferring some Baker and Adamson reagent grade SbCl_5 to graduated test tubes and diluting with concentrated HCl (Baker A.R.). Without the use of a dry box, the SbCl_5 reacts with the water vapor in the room and therefore, the volume of the SbCl_5 is only a rough estimation of the total SbCl_5 transferred. The optical density of the three solutions indicated that they did not contain the same concentration of SbCl_5 . Using an extinction coefficient of 7.84×10^3 for SbCl_6^- (47) the concentrations were found to be 0.12 M within 20 per cent. The difference in concentration is not expected to interfere with the comparison of the half-times.

Table 3
Half-times for Hydrolysis of SbCl_6^- in HCl

M, HCl	Temp	$T_{1/2}$ (min.)
9	25	35
6	25	80
5.93	16	284
5.96	16	286
5.87	25	88
4.72	25	126
2.38	25	252
1.19	25	322
1.18	16	820
0.47 (pH = 0.4)	25	277
0.0047 (pH = 2.4)	25	189
0.00024 (pH = 3.6)	25	98

The majority of runs were made by injecting 100 microliters of SbCl_6^- stock solution into 100 ml. of buffered solution. The buffers consisted of 0.1M HCl , $\text{HC}_2\text{H}_2\text{O}_2\text{Cl}$, $\text{HC}_2\text{H}_3\text{O}_2$, H_3PO_4 , NaH_2PO_4 , Na_2HPO_4 , H_3BO_3 , and Na_2CO_3 adjusted to the desired pH, using a Beckman pH meter, by 0.1 M NaOH . The hydrolysis reaction was then followed on a Beckman model DU spectrophotometer using fused silica cells having a light path of one cm. The cells were maintained at constant temperature by means of a water jacket, through which water from a thermostated bath ($25.0 \pm 0.4^\circ$) was circulated. Some of the runs were followed on a Beckman Model DK recording spectrophotometer in which case the temperature was not controlled and was greater than 25°C .

Data were taken at time intervals dependent on the rate and the wave length. For the faster reactions data were taken at short intervals, normally six minutes apart. For the slower reactions and for wave lengths other than the one of maximum absorption data were taken at longer intervals. Except for the extremely fast reactions and the DK runs each point is an average of three readings. In most of the buffers the reaction was first-order or pseudo first-order, as indicated by the linearity of plots of $\log (A - A_{\infty})$ vs time, where A represents the absorbancy or optical density at time t . A pseudo first-order reaction would be indistinguishable from a first-order reaction since the hydronium and hydroxyl ion concentrations were constant during any particular run. The chloride ion concentration is considered to be the same (except for Runs 33 and 34 in which additional HCl was added) from run to run although no attempt was made to determine,

precisely, what the concentration was. The half-times were calculated from the slopes of the plots.

Results.--The results are presented in Table 4 and plots of several runs are shown in Figure 5. Where results were obtained from the DK spectrophotometer, it is designated as such in the temperature column. Of the runs shown in Figure 5, Nos. 22, 23 and 26 were followed at 266.5 m μ . Runs 1 and 31 were followed at 270 m μ ; the difference in absorbancy is due to use of different stock solutions.

It was contemplated that the various buffering media would have no effect on the hydrolysis other than that expected by the hydronium ion; however, results tend to disprove this theory. When the hydrolysis is performed in the H_3BO_3 - NaOH buffer and the ensuing data plotted, the graph exhibits a curved rather than a straight line. The results of two runs are plotted in Figure 6. Attempts to fit the data to an integral order rate failed as the data fell between zero and first-order. The possibility of the curved line being due to a specific effect of the borate buffer was investigated by replacing the boric acid with glycine as a buffer component. Runs No. 22, 23, and 26 which contained glycine are shown in Figure 5, and although No. 26 exhibits a detectable arc, it is definitely not as pronounced as the arc obtained if H_3BO_3 is one of the buffer components at the same pH. For runs where curvature was obtained, two values are given in the half-time column of Table 4: (1) the half-time corresponding to the initial slope, and (2) that corresponding to the slope at the time that the reaction is 50 per cent complete.

Table 4

Half-times for Hydrolysis of SbCl_6^- in Various Buffered Solutions

Run	pH	Temp	Buffer	λ	$t_{1/2}(\text{min.})$
32	1.36	25°C	HCl	270	280
33	1.89	25°C	HCl	270	153
34	2.16	25°C	HCl	270	180
31	2.79	25°C	$\text{HC}_2\text{H}_3\text{O}_2 + \text{NaOH}$	270	338
30	5.00	25°C	$\text{HC}_2\text{H}_3\text{O}_2 + \text{NaOH}$	270	310
30	5.00	25°C	$\text{HC}_2\text{H}_3\text{O}_2 + \text{NaOH}$	300	310
29	6.98	25°C	$\text{NaH}_2\text{PO}_4 + \text{NaOH}$	270	168
29	6.98	25°C	$\text{NaH}_2\text{PO}_4 + \text{NaOH}$	290	165
1	7.65	25°C	$\text{NaH}_2\text{PO}_4 + \text{NaOH}$	270	129
7	7.82	25°C	$\text{H}_3\text{BO}_3 + \text{NaOH}$	266.5	120(109)
26	8.69	25°C	Glycine + NaOH	266.5	108(96)
10	8.91	25°C	$\text{H}_3\text{BO}_3 + \text{NaOH}$ (a)	266.5	72(45)
23	9.15	25°C	Glycine + NaOH	266.5	31
5	9.20	29°C	$\text{H}_3\text{BO}_3 + \text{NaOH}$	266.5	64(32)
9	9.22	28°C	$\text{H}_3\text{BO}_3 + \text{NaOH}$ (a)	266.5	42(21)
8	9.35	28°C	$\text{H}_3\text{BO}_3 + \text{NaOH}$	266.5	57(22)
21	9.59	DK	$\text{H}_3\text{BO}_3 + \text{NaOH}$ (a)	peak	13.6(8.5)
22	9.60	26°C	Glycine + NaOH	266.5	15.5
6	9.80	25°C	$\text{H}_3\text{BO}_3 + \text{NaOH}$	266.5	43(15)
19	10.06	DK	$\text{Na}_2\text{HPO}_4 + \text{NaOH}$ (a)	peak	8.8

18	10.51	DK	Na_2CO_3 (a)	peak	1.1
17	11.0	DK	$\text{Na}_2\text{HPO}_4 + \text{NaOH}$	peak	1.4
3	11.2	25°C	$\text{Na}_2\text{HPO}_4 + \text{NaOH}$	266.5	1.75
11	12.40	25°C	NaOH	266.5	very rapid

(a) 10 cm. cell 0.01M SbCl_6 stock solution

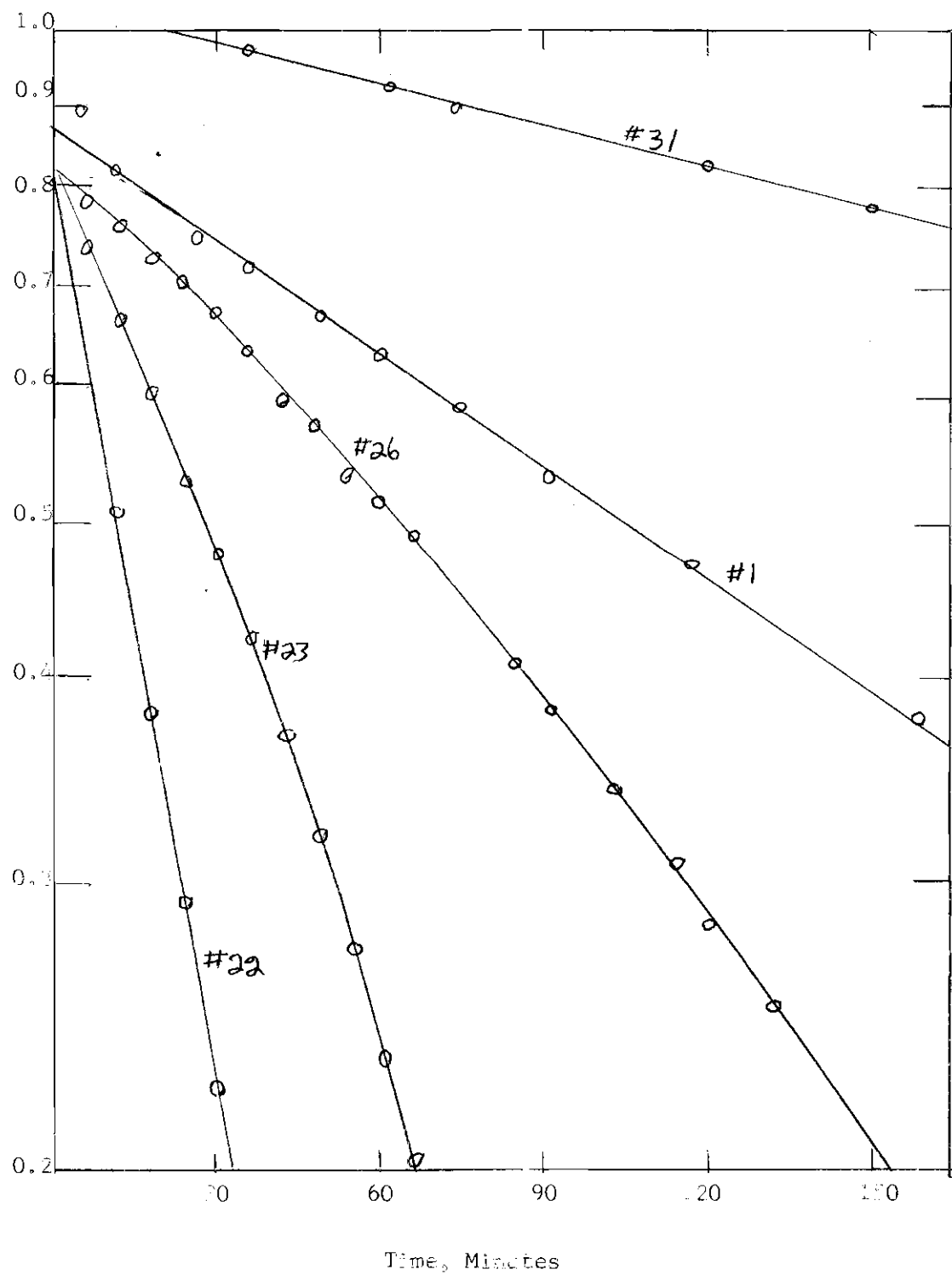


Figure 5. Plot of Absorbance of SbCl_6^- vs Time.
(Runs 1, 22, 23, 26, and 31).

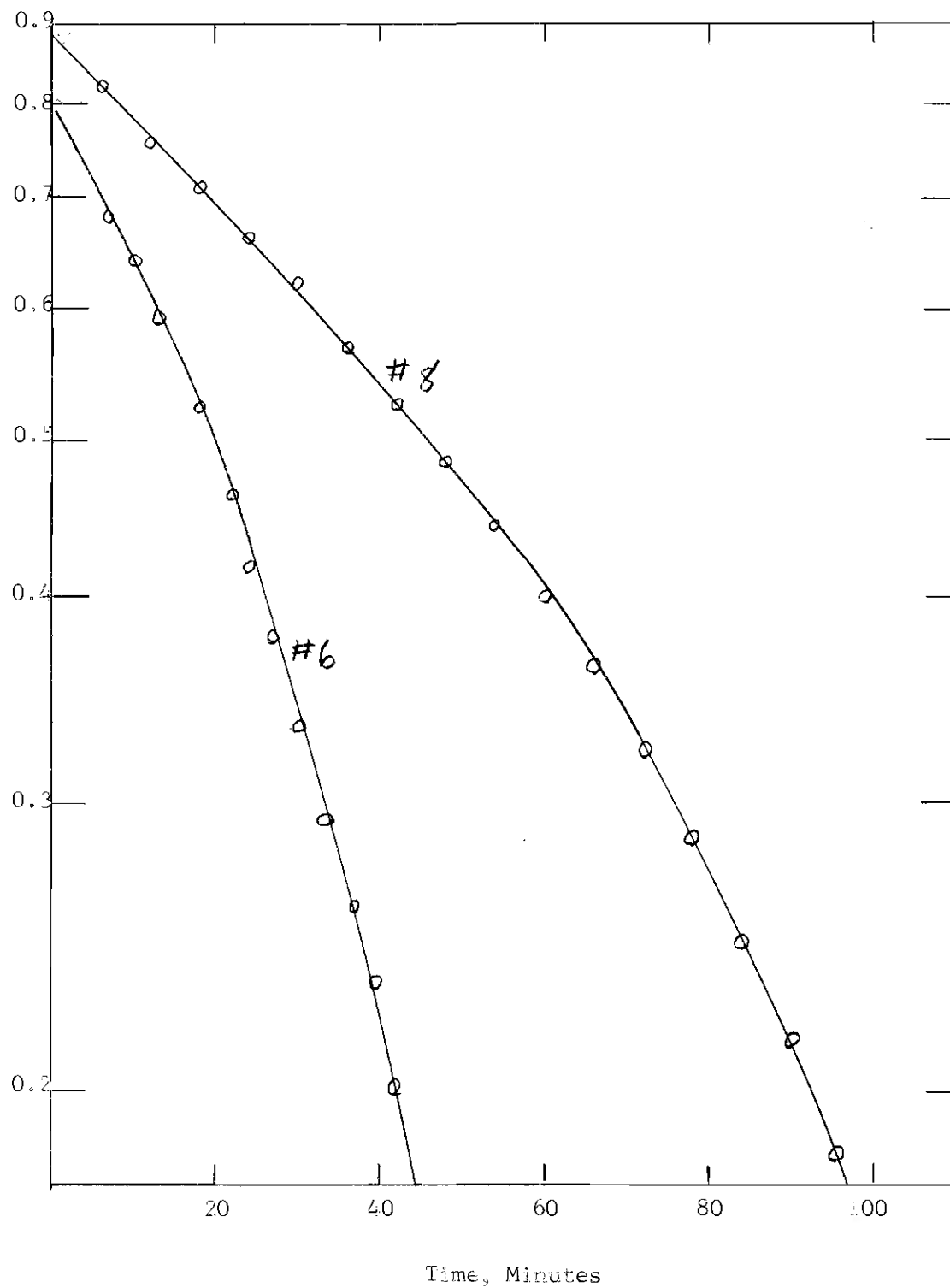


Figure 6. Plots of Absorbancy of SbCl_6^- in H_3BO_3^- NaOH Buffers vs Time. (Runs 6, 8).

It was next considered that the curvature might result from the presence of appreciable amounts of $\text{Sb(OH)}_5\text{Cl}^-$ during certain periods of the reaction. Although $\text{Sb(OH)}_5\text{Cl}^-$ is known to show appreciable absorption in the region of 270 $\text{m}\mu$, the earlier work in acid solution (48) indicated that $\text{Sb(OH)}_5\text{Cl}^-$ is rapidly hydrolyzed and does not accumulate during the reaction. The entire spectrum was scanned by use of the recording spectrophotometer in a run involving a borate buffer (Figure 7), but there was no evidence of increased absorption in the region of maximum absorption for $\text{Sb(OH)}_5\text{Cl}^-$.

The problem of whether the observed peak, generally attributed to SbCl_6^- , is actually due to more than one species has been studied by Bonner and Goishi (49). They found that the zero-time spectra in 7M and 12M HCl were appreciably different, but that there was very little change in the spectra in solutions 1.2M to 7.69M in HCl. They concluded that a large solvent effect was more probable than the presence of two or more species.

If the observed peak results from the presence of two species, different rates of hydrolysis should be obtained by plotting data obtained at different wave lengths provided any equilibrium between the species is not reached rapidly relative to the rate of hydrolysis, and provided the spectra are sufficiently different. The half-times for the hydrolysis reaction taken at 270 and 290 $\text{m}\mu$ during the same run were found to be the same within experimental error. Some values are given in Table 4 for Runs 29 and 30.

If the equilibrium between the two species is established rapidly, the reaction would appear to be first-order and the same rate

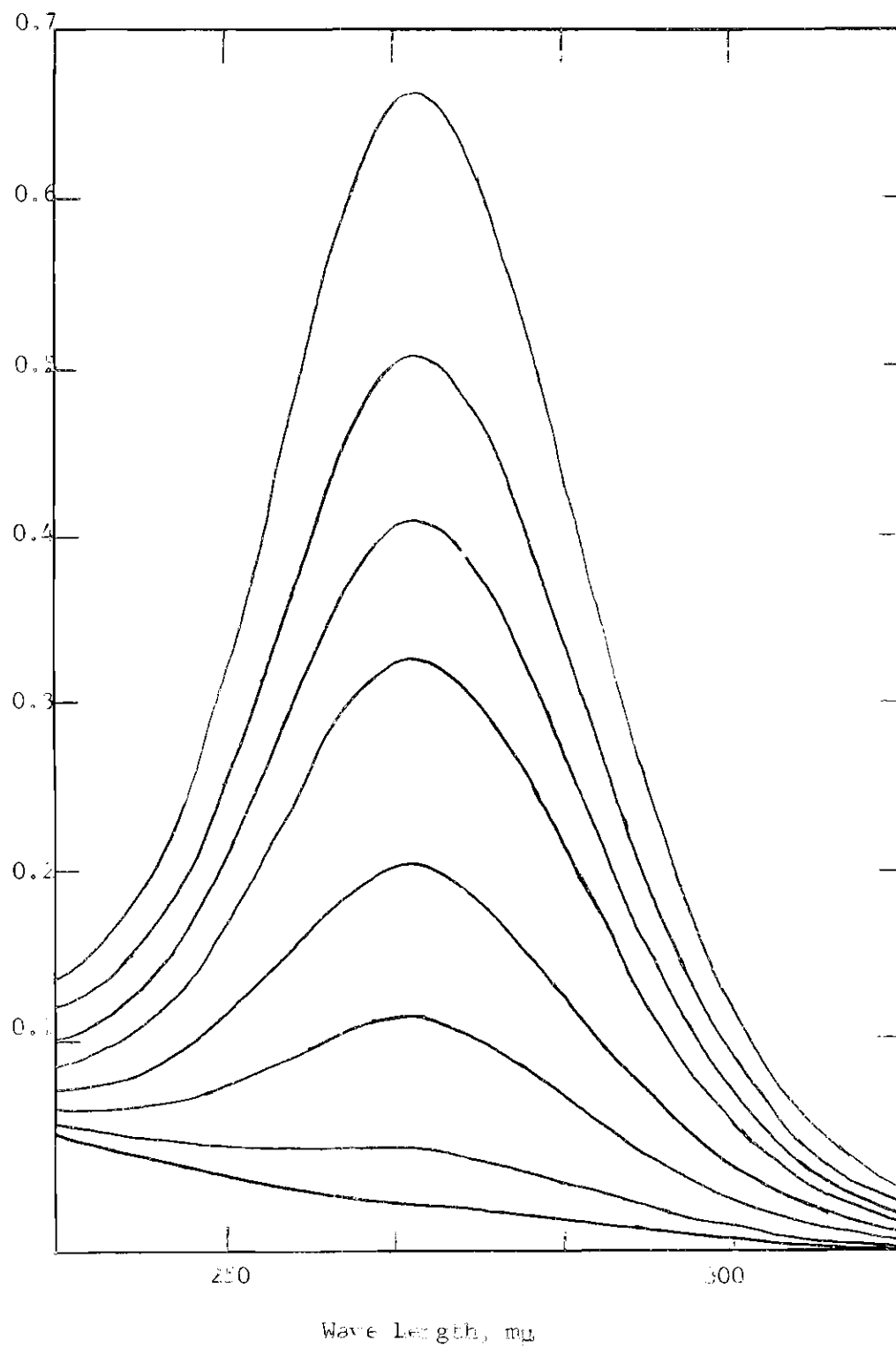


Figure 7. Absorbance of StCl_6 during Hydrolysis. (Run No. 12.)

would be obtained at all wave lengths. If such were the case it would be possible to gain some insight as to the relative concentration of the two species by taking the ratios of the absorbancies, A , at say 270 $m\mu$ and 300 $m\mu$ in one solution and comparing it to the ratio in another solution; i.e.,

$$\frac{A_{270}}{A_{300}} = \frac{C_1 E_1^{270} + C_2 E_2^{270}}{C_1 E_1^{300} + C_2 E_2^{300}}$$

where the C 's are the concentrations and the E 's are the molar absorbancy indexes of the species. The subscripts represent species 1 and 2 respectively. Here it is necessary that the ratios $\frac{E_1^{270}}{E_1^{300}}$ and

$\frac{E_2^{270}}{E_2^{300}}$ are sufficiently different

Table 5

Ratios of A_{270}/A_{300}			
	A_{270}	A_{300}	A_{270}/A_{300}
12M HCl	0.831	0.238	3.6
pH			
5	1.06	0.214	5.0
8.2	0.960	0.192	5.0
9.18	0.950	0.198	4.8
9.2	0.892	0.185	4.8

Values for absorbancy ratios are presented in Table 5 and it can be

seen that the value in 12 M HCl is at least 25 per cent different from the other values which are the same within an estimated ± 0.3 error.

In summary the facts pertaining to solutions in the pH range 1-12 are: (1) there is no shift in the position of the absorption peak, neither during a run nor from one solution to another, (2) the absorbancy ratios at 270 and 300 μ are the same within an estimated ± 0.3 , (3) the half-times of hydrolysis derived at different wave lengths are the same, and (4) a plot of $A-A_{\infty}$ vs time yields a straight line (except for Run No. 26 and possibly Run No. 23). It is concluded that in the pH range of these experiments the rate being measured is that of the hydrolysis of the single species SbCl_6^- .

Since the rate of hydrolysis is greatly accelerated in strong acid or base, the rate constant might be expected to be given by the expression:

$$k_o = k_1 + k_2[\text{H}^+] + k_3[\text{OH}^-] = k_1 + k_2[\text{H}^+] + \frac{k_3 k_w}{[\text{H}^+]}$$

if the activity coefficients remained constant. The derivative of k_o with respect to $[\text{H}^+]$ is

$$\frac{dk_o}{d[\text{H}^+]} = k_2 - \frac{k_3 k_w}{[\text{H}^+]^2}$$

The value of the derivative is zero at a minimum point and from the expression it is seen that there is only one minimum point if there are no other factors.

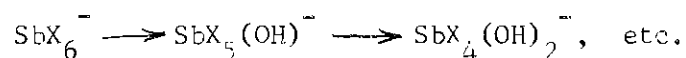
Using the data of Tables 3 and 4 a plot of rate vs. pH was

attempted, but the considerable scatter of the points did not lead to a reliable curve. Two minimum points, one between pH 1.36 and -1.1 and one between pH 1.36 and 2.16, are indicated. The behavior in HCl solutions indicates an effect due to variations in the activity coefficients of SbCl_6^- . It is known that the activity coefficient of HCl has a minimum value in 0.5 M HCl. If we assume that the activity coefficient of SbCl_6^- follows the same type of behavior in the same pH range, we can impose this effect on the expected rate vs. pH curve to account for two minima. The effect of the various buffers on the ionic strength and activity coefficients of SbCl_6^- (and possibly on the activity of water) are probably the cause of the inability to gain a smooth curve over the entire pH range. However, the effect on activity coefficients is not as great as the effect of pH, and it can definitely be stated that increase in basicity beyond the minimum point greatly accelerates the reaction.

CHAPTER V

DISCUSSION

All evidence of the replacement reactions of the halo complexes of Sb(V) suggest that these complexes hydrolyze in a step-wise fashion



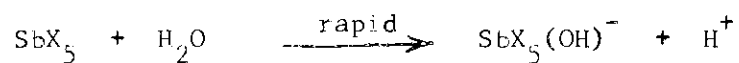
although some steps may be immeasurably fast. The complexes formed are then mixed halo-hydroxo complexes, there being no evidence for mixed halo-aquo complexes in either the fluoro- (46) or chloro- (48, 49) systems.

The hydrolysis of an ion of the type SbX_6^- may proceed by a variety of mechanisms. The possible mechanisms can be divided into two groups, on the basis of whether they are fundamentally of the $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ type. The mechanisms which are of the $\text{S}_{\text{N}}1$ type are:

(1) Simple $\text{S}_{\text{N}}1$ mechanism involving a five-coordinate Sb as an intermediate; i.e.,



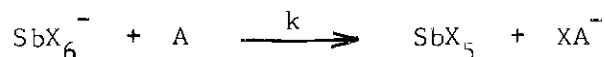
followed by rapid reaction of the five-coordinate SbX_5



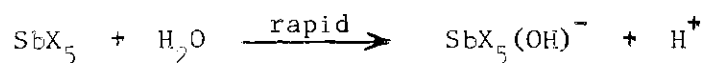
In this mechanism the reaction would be first-order, and the rate would

be independent of pH.

(2) Electrophilic removal of X^- to yield a five-coordinate Sb as an intermediate; i.e.,

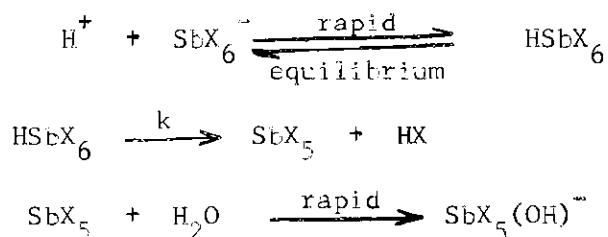


again followed by the rapid reaction of SbX_5 .



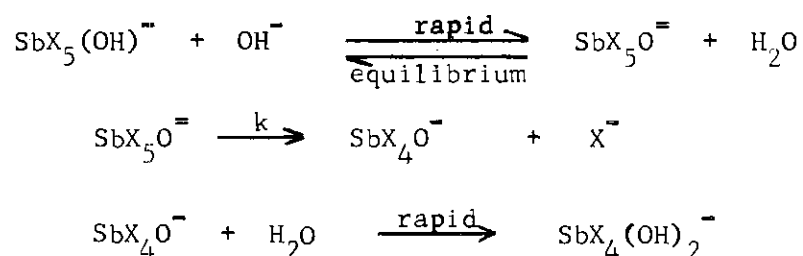
In this mechanism the reaction would be second-order, and will be dependent on the pH in so far as the latter affects the concentration of A. In the case of $SbCl_6^-$ hydrogen ion itself serves as A, so that the rate of hydrolysis increases with increasing acidity. Some evidence suggests that $SbCl_3$ can serve as A. (2)

(3) A mechanism related to (2) in that A forms an intermediate which is more than just a transition state. For example, a true halo-acid may be formed if the hydrogen ion again serves as A; i.e.,

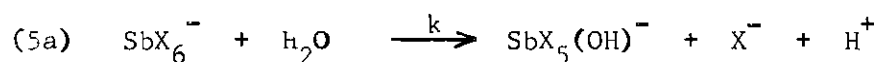


This mechanism is kinetically indistinguishable from mechanism (2) if the equilibrium concentration of $HSbX_6$ is small.

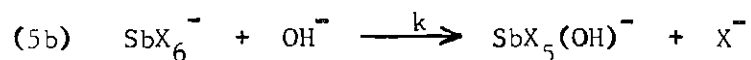
(4) An S_N1CB mechanism, in which the reaction intermediate is the conjugate base of the ion undergoing hydrolysis, is possible for a mixed halo-hydroxo complex although it is not possible for SbX_6^- .



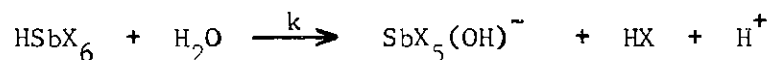
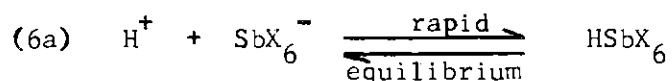
The mechanisms which are of the S_N2 type will be variations of those previously considered, with either H_2O or OH^- acting as the nucleophilic reagent.



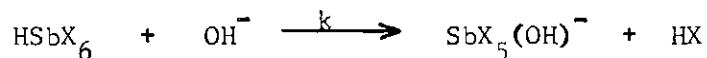
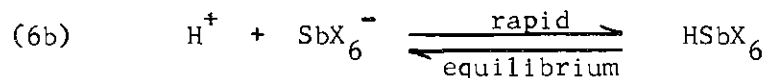
In this mechanism the reaction will be pseudo-first-order, and will be independent of pH.



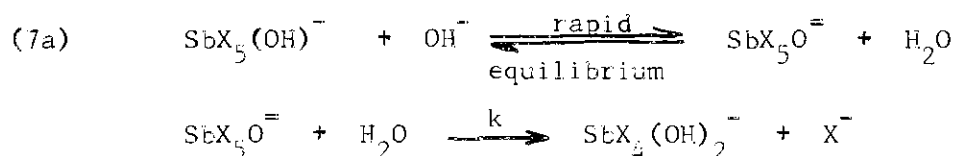
In this mechanism the reaction will be second-order, and the rate of hydrolysis will increase with increasing basicity.



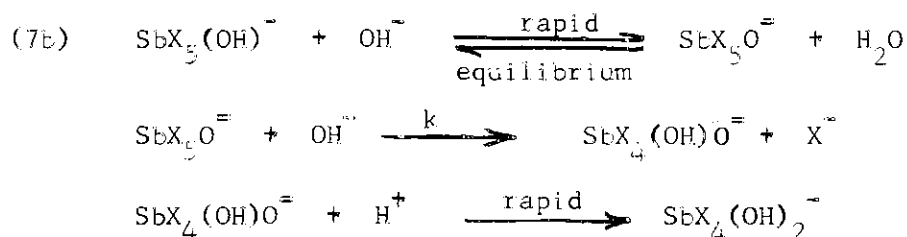
In this mechanism the reaction will be pseudo-second-order, and the rate of hydrolysis will increase with increasing acidity.



In this mechanism the reaction will be independent of pH.



In this mechanism the reaction will be pseudo-second-order, and the rate of hydrolysis will increase with increasing basicity.



In this mechanism the reaction will be third-order, and the rate will increase with increasing basicity.

Although all the various mechanisms may be operative in both the SbF_6^- and SbCl_6^- systems, there are enough obvious differences to suggest that the major paths of reaction are different in the two systems. The chief difference is the fact that in the chloro case the first step is measurable and the following steps are very rapid, while in the fluoro case the reverse is true. This difference might well be due to differing tendencies to react via an $\text{S}_{\text{N}}1$ as opposed to an $\text{S}_{\text{N}}2$ mechanism.

To indicate the likelihood of a difference of this kind the octahedral species will be considered from the point of view of whether the complex is more likely to undergo increase or decrease in coordination number. From the known facts it would appear that the fluorides of Sb(V) have a greater tendency to form a higher coordination number than the chlorides. For instance, liquid SbF_5 , a viscous material, is polymeric in nature and forms long chains of octahedral SbF_6 groups (21)

indicating its reluctance toward coordination number five. On the other hand SbCl_5 is not viscous, and consists of discrete molecules in the liquid state. The structure of SbCl_5 , proposed by Moureau, Sue, and Magat (50), on the basis of the Raman spectrum, is a trigonal bipyramid in which the Sb(V) is displaced from the plane of the three chlorides. There is even a suggestion in the literature for a coordination number of four for Sb(V) . Usanovich, Sumarokova, and Beketov (51) attributed the results of their conductometric, viscosity, and density measurements on SbCl_3 - SbCl_5 mixtures to formation of the ion-pair $\text{SbCl}_4^+ \text{SbCl}_4^-$.

A few complexes having a coordination number of seven are known, and most of these involve fluoride as a ligand. These complexes are UF_7 , UO_2F_5^- , and ZrF_7^- , which have the form of a pentagonal bipyramid, and TaF_7^- , NbF_7^- , and NbOF_6^- , which have the form of a distorted trigonal prism (52). If we relate size of the central atom to the tendency for greater stabilization of the seven coordinate species, we can show in Table 6 that the size of Sb^{+5} is in the region where stabilization of coordination number seven would be expected. Since it is not clear which of the many "size" values is most appropriate, and because one set of "radii" does not include all of the elements of interest, several "radii" are listed. The values are from Kleinberg, Argersinger, and Griswold (53).

On the basis of these arguments an $\text{S}_\text{N}1$ reaction seems more probable for SbCl_6^- , and an $\text{S}_\text{N}2$ reaction seems more probable for SbF_6^- .

The central atoms P^{+5} and As^{+5} have been included in Table 6 since some information is available on the behavior of PF_6^- and AsF_6^- . Both of these ions are known to resist hydrolysis in base over extended

Table 6

Ionic and Covalent Radii

	ionic crystal radius (calc.)	ionic crystal radius (empirical)	ionic univalent radius (calc.)	covalent single bond radius
P ⁺⁵	0.36		0.62	1.10
As ⁺⁵	0.46		0.70	1.21
I ⁺⁷	0.50		0.77	1.334
Sb ⁺⁵	0.63		0.90	1.41
Nb ⁺⁵	0.70		1.00	1.342
Ta ⁺⁵		0.73		1.343
Zr ⁺⁴	0.80	0.87	1.09	1.454
U ⁺⁶	0.83			1.421

periods of time (4,30). The sizes listed in Table 6 suggest that phosphorus and arsenic are too small to permit expansion to coordination number seven, and therefore hydrolysis by an S_N2 type of reaction is unlikely. Of course, the observed resistance to hydrolysis also implies that the S_N1 reactivity is small.

The radius ratio of ligand ion to central ion in $SbCl_6^-$ is about what the ratio is in AsF_6^- , so that the reactions in these two systems would be expected to be similar. A point of similarity is that $AsF_5(OH)^-$ hydrolyzes more rapidly than AsF_6^- , just as $SbCl_5(OH)^-$ reacts more rapidly than $SbCl_6^-$. Hydrolysis of $AsF_5(OH)^-$ is catalyzed by both acid and base. Unfortunately, Dess and Parry (4) do not report whether acid has any effect on the hydrolysis of AsF_6^- .

The progressive change in rate on replacing halide with hydroxide is consistent with what has been said so far. In the $SbCl_6^-$ and AsF_6^- systems, which appear to proceed by an S_N1 mechanism, the replacement of a halide with hydroxide leads to a faster rate of hydrolysis. A few systems, involving other central atoms, are available for comparison. The rate of hydrolysis of chlorohydroxo complexes of **Co(III)** are faster than those of the corresponding dichloro complexes by a factor of 40 to 50 (1). In the case of carbon as the central atom, $CH_2Cl(OH)$ cannot be compared to CH_2Cl_2 , but the solvolysis of $CH_2Cl(OCH_3)$ is much more rapid than that of CH_2Cl_2 (54). The evidence in the case of carbon and cobalt points to the reactions being of the S_N1 type. Reactions of the S_N1 type are facilitated by the presence of groups which release electrons to the reaction center, and

this release is generally attributed to the possibility of π bonding (1,55). Using the values of σ_R given by Taft (56) as a measure of the effect of groups via their π bonding tendency we would expect the following order of reactivity: $\text{OH} > \text{F} > \text{Cl}$. On the other hand, if the inductive effect of the group is more important, then the ordering predicted is $\text{OH} > \text{Cl} \sim \text{F}$. In either case hydroxide would be expected to labilize the reaction with respect to chloride. Examination of mixed chloro-fluoro complexes would appear to be desirable to decide which effect is more important. All the arguments presented do suggest that SbCl_6^- and AsF_6^- react by an $\text{S}_\text{N}1$ mechanism in acid solution.

On the other hand reactivity via the $\text{S}_\text{N}2$ mechanism would be expected to be diminished by the presence of groups with electron releasing characteristics. In such systems replacement of halide by hydroxide would be expected to lead to diminished rates. This is what is observed in the SbF_6^- system.

The behavior of SbCl_6^- may now be summarized. The studies of Neumann and Ramette (2) establish an acid dependent mechanism, which could be (2), (3) or (6a), but which is probably (2). In addition these studies indicated that a pH-independent mechanism is operative and this could be mechanism (1), (5a), or (6b), but is probably (1). The present work appears to establish the $\text{S}_\text{N}2$ mechanism (5b) as another pH dependent mechanism since the hydrolysis rate definitely increases with increasing basicity in the first step of the chloro case where mechanism (4) cannot be operative. In the region of the minimum rate all mechanisms are making some contribution to the reaction so that the rate constant is given by the expression

$$k = k_1 + k_2 [H^+] + k_3 [OH^-]$$

Using a value of k_2 from the experiments of Neumann and Ramette (2) in acid solution, and assuming that the rate of hydrolysis in the very basic region is due entirely to the third term, k_3 appears to be approximately 10^6 times k_2 .

Species of the type involved in mechanism (4) provide a possible explanation for the reactions of $SbCl_6^-$ that deviated from first-order kinetics. From the known spectral characteristics of the hydrolysis products it is clear that once $SbCl_6^-$ reacts it gives products containing three or less chlorides, and that any monomeric products are in equilibrium (48,49). In addition to products of the type $SbCl_x(OH)_{6-x}^-$, there may also be products of the type $SbCl_x(OH)_{5-x}O^-$. Products of the latter type will be relatively more abundant at high pH values. A species of this type might act as a nucleophilic reagent, thus providing an auto-catalytic effect on the hydrolysis of $SbCl_6^-$. A reaction of this type could also account for formation of polymeric species such as that indicated in the fluoride system. At even higher pH, reaction (5a) has priority and polymeric substances would be avoided.

In the fluoro case many variants may be suggested. However, we have at present no experimental evidence to distinguish between mechanisms, so we confine ourselves to the suggestion that the probability of S_N2 reaction for the second step is much less than in the first step, etc., while the probability of S_N1 reaction increases from step to step. The increase in rate at the fourth step may then be due

to a change to an S_N1 mechanism. The formation of a polymeric material after the fourth step would then close the avenues of reaction.

For future consideration, it is suggested that exchange reactions be performed in order to determine the relative lability of F^- and OH^- in the SbF_6^- system. Also, the rate of the fourth step of fluoride replacement should be examined. This would necessitate the detection of the various species in solution. Perhaps this resolution could be accomplished by a variation of the chromatographic method of Kolditz and Sarrach, or through the use of NMR measurements. Further, more detailed analysis of the rates should be made in limited pH regions where the activity coefficients could be held constant by use of solutions of constant ionic strength.

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